A STUDY OF THE TRANSFERENCE PROPERTIES OF POLYMERIC ELECTROLYTES USING RADIOACTIVE TRACERS

BY

JOHN ROBERT HUIZENGA

A.B., Calvin College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

A STUDY OF THE TRANSFERENCE PROPERTIES OF POLYMERIC ELECTROLYTES USING RADIOACTIVE TRACERS

BY

JOHN ROBERT HUIZENGA

A.B., Calvin College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ACKNOWLEDGMENT

The author takes this opportunity to express his sincere appreciation to Professor F. T. Wall, under whose direction this investigation was carried out. He is also indebted to Dr. P. F. Grieger for many helpful discussions on various phases of the work.

The necessary radioactive isotopes were kindly supplied by the Atomic Energy Commission of Oak Ridge, Tennessee and by Professor A. L. Hughes and his cyclotron group of Washington University, St. Louis, Missouri.

R. UNIV.
BIBLIOTHEEK
LEIDEN

A STUDY OF THE TRANSFERENCE PROPERTIES OF POLYMERIC ELECTROLYTES USING RADIOACTIVE TRACERS

Introduction

A considerable amount of evidence available at the present time indicates that in aqueous mixtures of polyacrylic acid and sodium hydroxide, sodium ion is associated with polyacrylate ion to an important extent. The results of Kern (1,2) as well as other measurements made in this laboratory (3,4) are in qualitative agreement on this point. However, they are in quantitative disagreement, so additional experimental information is required to clarify the situation.

Three different types of experiments have been developed which will yield information on ion association in aqueous mixtures of polyacrylic acid and sodium hydroxide. These are:

a) Hittorf transference experiment (using radioactive sodium to determine the flow of sodium) combined with conductance measurements.

b) Self-Diffusion experiments.

c) Transference experiment when the ion exchange rate is finite.

Some of the other important properties of the polymeric anion deduced from the above experiments are the equivalent conductance, transference number, charge and mobility.

Discussion Of Results

Partially neutralized polymeric acids exhibit properties which are peculiar to high molecular weight compounds. One of the most interesting properties of solutions of polyacrylic acid and sodium hydroxide is the association of sodium ions with polyacrylate ions. This fraction of bound sodium may be experimentally determined by combining data obtained from

a Hittorf type transference experiment with pH and conductance measurements. Since previous attempts (1,2,3,4) to measure the fraction of bound sodium are in extremely poor agreement, and since transference results are roughly midway between the other estimates, it appeared worthwhile to test the validity of the transference experiments in another way. This was accomplished by measuring the diffusion of radioactive sodium in otherwise uniform solutions of polyacrylic acid and sodium hydroxide, using the steady state technique (5,6). The results obtained from the diffusion experiments are in excellent agreement with the transference results. For comparison, the results of Stent obtained by using sodium amalgam electrode-E.M.F. measurements and of deButts obtained by repeating the pH and conductance measurements of Kern are included in Table I. The transference number, t_p, and the equivalent conductance, Λ_p, of the polyacrylate ion also appear in Table I.

TABLE I.

0.0378 N. Polyacrylic Acid

% Neutralization	Bound Sodium Fraction				t_p	Λ_p
	deButts	Stent	Diffusion	Transference Conductance		
9.60	0.00	0.78	0.12	0.14	0.31	24
24.0	0.00	0.89	0.29	0.27	0.42	34
41.3	0.00	0.90	0.41	0.41	0.46	40
61.7	0.06	0.87	0.51	0.54	0.49	45
81.6	0.25	0.80	0.59	0.60	0.49	44
97.9	0.40	0.73	0.62	0.62	0.43	34

As can readily be seen from the above Table, the polymer ions conduct nearly one-half the current in the range 25 to 100 percent neutralization whereas in pure acid solutions hydrogen ions carry virtually all the current. deButts (3) assumed that a negligible fraction of the current was carried by the partially neutralized polymer ion in his calculation. In

consequence, it is easily understood that his results are much too low.

The equivalent conductance of the polyacrylate ion is relatively high and seems to reach a maximum in the neighborhood of 60 percent neutralization, although the charge on the ion increases monotonically. The maximum is not surprising since as the charge on the polyacrylate ion increases, the effective volume of the ion is expected to increase due to the intraionic electrical repulsion. Substantiating this view the "rational mobility" of the polyacrylate ion has been found to decrease monotonically as ion charge increases. Hence the increase in the equivalent conductance is less than proportional to the polyacrylate charge over the entire range of neutralization, and finally over the range 60 to 100 percent neutralization the volume effect becomes large enough to cause a decrease in the equivalent conductance.

With increasing neutralization, the polyacrylate ion associates a larger and larger percentage of each added increment of sodium ions up to 80 percent neutralization. At 61.7 percent neutralization, the fraction of sodium associated with the polyacrylate ion was found to be approximately constant over the concentration range 0.0151 N. to 0.1189 N. polyacrylic acid. Diffusion results showed a smaller fraction of sodium associated in 0.00378 N. polyacrylic acid. A priori one would expect smaller fractions of bound sodium in the more dilute solutions.

In the case of polyacrylic acid - sodium hydroxide mixtures the exchange rate of sodium between polyacrylate ion and sodium ion has been found to be finite. Therefore for transference experiments of type (a) to be valid, the initial solution should be uniform throughout, not only with respect to the stoichiometric concentrations of the principal chemicals involved (polyacrylic acid and sodium hydroxide in the present case) but also with respect to tracer concentration.

Transference experiments, type (c), with an initial discontinuity in tracer concentration have also been carried out. The interpretation of these experiments involves the solution

of two differential equations which both contain the flow of tracer and the finite exchange constant.

BIBLIOGRAPHY

1. Kern, Werner, Z. Phys. Chem. *A181* 249, 283 (1937-38)
2. Kern, Werner, Z. Phys. Chem. *A184* 197, 302 (1939)
3. deButts, E. H. Jr., Ph.D. Thesis, University of Illinois (1948)
4. Stent, G. S., PhD. Thesis, University of Illinois, (1948)
5. Brady, and Salley, J. A. C. S. *70* 914 (1948)
6. Gordon, Annals New York Acad. of Science, *46* 285 (1945)

VITA

The author was born in Fulton, Illinois on April 21, 1921. His elementary and secondary education was acquired in the public schools of Illinois. In the fall of 1940 he enrolled at Calvin College in Grand Rapids, Michigan. He studied at the University of Illinois the summer semester of 1943. In February of 1944 he completed work for the degree of Bachelor of Arts. He then entered the Graduate College of the University of Illinois but left soon after for the Manhattan Project at Oak Ridge, Tennessee where he spent two years as a Laboratory Supervisor. In March 1946 he re-enrolled at the University of Illinois with the aid of a University Fellowship. From September 1946 to June 1947, he was an instructor in chemistry at Calvin College. He returned to continue his graduate studies at the University of Illinois in June 1947 as a University Fellow. He later held a teaching assistantship in the Physical Division for two semesters. During the fall semester of the academic year 1948-9 he was a Graduate Fellow, and during the spring semester he was employed as a special research assistant under contract with the Rubber Reserve Corporation.

The author is a member of Phi Beta Kappa, Sigma Xi, Phi Kappa Phi, Phi Lambda Upsilon, Pi Mu Epsilon, Alpha Chi Sigma, and the American Chemical Society.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549807_0059